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(54) **Moisture corrosion inhibitor layer for Al-alloy metallization layers, particularly for electronic devices and corresponding manufacturing method**

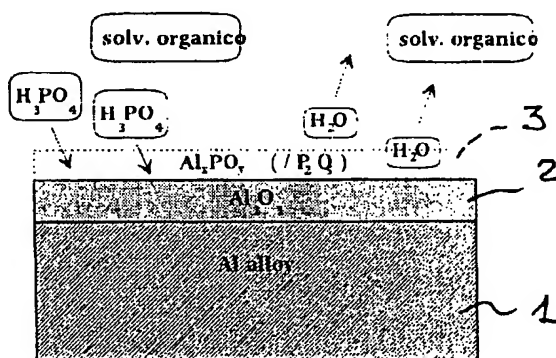
(57) The invention relates to a method of producing a protective inhibitor layer of moisture-generated corrosion for aluminum (Al) alloy metallization layers (1), particularly in semiconductor electronic devices.

The method of this invention comprises chemically treating the metallization layer (1) in at least two steps using a mixture of concentrated nitric acid and trace phosphoric acid, in order to produce a thin protective phosphate layer (3).

Alternatively, the method comprises dipping the

electronic device at least once in a mixture of a polar organic solvent and phosphoric acid ( $H_3PO_4$ ) or phosphate derivatives thereof in low percent amount, e.g. with a phosphate reactant such as orthophosphoric acid or even  $R-H_xPO_y$ , where R is an alkaline type of ion group or an alkyl radical.

The thin film (3) is formed on top of a thin layer (2) of native aluminum oxide hydrate  $Al_2O_3 \cdot xH_2O$ .



**Fig. 1b**

## Description

### Field of the Invention

[0001] This invention relates to an inhibitor layer for inhibiting moisture-generated corrosion of Al alloy metallization layers employed in microelectronic devices, and to a method of fabricating such a layer.

[0002] The invention also relates to a method of fabricating this layer as well as semiconductor integrated electronic devices incorporating the layer.

[0003] As is well known in this specific field, corrosion of the final metallization layer, mainly occurring when the electronic devices are assembled and encapsulated in plastics packages, represents a serious problem of reliability in the manufacture of semiconductor integrated electronic devices.

[0004] For example, the performance of power devices incorporating MOS power transistors is deeply affected by corrosion of the metal layer on the device face. This effect is the more strongly felt the smaller the dimensions of the integrated circuit.

[0005] A determining value for satisfactory operation of the device is its resistance in the power-on condition, and this value can be deeply altered by oxidation of the metal layer on the device face, which layer is, in power devices, coincident with the source electrode of the power MOS. Face metallizing is common practice in the semiconductor industry, and involves depositing a layer of an aluminum alloy, typically Al-Si (1% w/o), in all those devices for which electromigration is of no serious concern, such as in power switches using power MOSs.

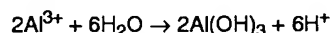
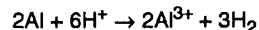
[0006] The corrosive phenomenon in a damp environment can start at the surface of the Al-Si alloy whenever condensation water collects thereon, since water contains a sufficient concentration of corrosive ion impurities dissolved in it. Condensation water can also form locally on the metal layer surface, e.g. as a result of water penetrating the package and the molding protection resin during the tests for operability in moisture, occasionally carried out inside pressure cookers.

[0007] Certain ion species flowing between the cathodic and the anodic surface regions may be released from the molding resin itself, or may be contained as contaminants in the materials entering the construction of the integrated circuit. The molding resin, further to absorbing and possibly becoming saturated with water, can act somehow as an electrolytic medium, although the diffusion of ions and electrons through the resin layer meets with sufficient difficulty to retard and ultimately check the corrosive processes.

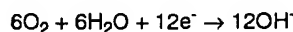
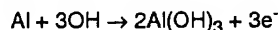
[0008] Finally, it should be noted that an electrolytic cell may form on the alloy layer surface. Its cathode and anode usually are two electrodes of the device, e.g. the gate and source metal contacts in a MOS power transistor, or may be the gold bonding wire and the surrounding surface of the Al metallization layer.

[0009] The Al metallization layer is normally coated

with a very thin (a few tens Å) layer of native oxide hydrate which preserves the metal beneath from further corrosion in standard environmental conditions. However, this native layer becomes eroded where the condensed electrolyte contains a sufficient amount of catalytic agents. In this case, the Al oxide hydrate is dissolved by chemical reaction, which results in the surface of the Al metal layer being rapidly brought to contact the electrolyte and a galvanic corrosion mechanism being initiated in the Al layer through either of two possible reaction paths, according to the local pH value: in an acidic medium,



and in a basic medium,



### Prior Art

[0010] A first prior approach to making corrosion less likely to occur is based on forming a suitable inhibitor layer over the surface of the aluminum alloy layer.

[0011] For this inhibitor layer to be effective, the layer and the processes for forming it are to meet certain requirements:

(a) be consistent with the performance of the finished device;

(b) leave the chemio-physical characteristics of the other layers comprising the integrated circuit unaffected;

(c) be compatible with the subsequent steps of bonding the lead wires and packaging.

[0012] In plastics packaged devices, the aluminum metal layer surface is generally "protected" with a relatively thick layer of a passivating dielectric (SiN, Pvpox, SiON, etc.) which prevents water from migrating to the aluminum surface from the molding resin. In all events, the passivating dielectric must be conformed, e.g. by a photolithographic process and associated etch, in order to bond wires to the surface of the Al metal layer and produce the contacts.

[0013] In power devices, where large currents are involved, bonding wires of diameters in the 2 to 20 mils range are usually employed which require a relatively broad bonding area.

[0014] The bonding ends represent uncovered metal regions and, accordingly, are potentially subject to the corrosive action of water in either saturated steam

or liquid form. It can be appreciated, therefore, that the passivation dielectric ordinarily employed cannot solve the problem in any conclusive way, and requires additional process steps (dielectric depositing, masking, etching) which introduce further problems from interaction with the underlying layers as well as added cost.

[0015] The technical problem underlying this invention is to provide a novel type of protection or passivation for the metal layers present in semiconductor integrated circuits, which exhibits appropriate structural and functional features to effectively protect the metal layer against corrosion, without burdening the electronic device manufacture with additional complexity and cost. In this way, the aforementioned drawbacks of the prior art can be overcome.

#### Summary of the Invention

[0016] The concept behind this invention is one of growing, over the metal layer, a very thin passivating phosphate layer or film effective to resist corrosion/hydroxidation of the metal when the latter is subjected to stresses in a damp environment. Preferably, this thin film is grown by chemical treatment of the Al alloy metal layer surface.

[0017] Based on this concept, the technical problem is solved by a corrosion inhibitor layer as previously indicated and defined in the characterizing portions of Claim 1 foll..

[0018] The invention also relates to a method of fabricating a corrosion inhibitor layer as defined in Claims 7 foll..

[0019] The features and advantages of the method and the inhibitor layer according to the invention will be apparent from the following description of embodiments thereof, given by way of non limitative example with reference to the accompanying drawings.

[0020] In the drawings:

#### Brief Description of the Drawings

[0021]

Figure 1A is an enlarged vertical cross-section view showing schematically a portion of a semiconductor electronic device subjected to a step of the inventive method.

Figure 1B shows schematically the substrate portion of Figure 1 at a subsequent step of the inventive method.

Figures 2 to 5 are XPS graphs or spectra illustrating schematically the results of test measurements, plotted as intensity vs. bonding energy for semiconductor electronic devices obtained in accordance with the inventive method.

#### Detailed Description

[0022] Referring to the drawing figures, in particular to Figure 1A, a metallization layer formed over a semiconductor electronic device, omitted from view because conventional, is generally shown schematically at 1. The metallization layer 1 may be an aluminum-silicon (Al-Si) alloy conventionally deposited as the final interconnection layer between electronic components integrated in a semiconductor integrated circuit.

[0023] The process steps and the structures described hereinafter do not describe a complete process for fabricating integrated circuits. The present invention, in fact, can be practiced concurrently with integrated circuit fabricating techniques presently employed in the industry, and only such process steps as are necessary to explain the invention will be discussed hereinafter.

[0024] Figures showing cross-sections through portions of an integrated circuit during its fabrication are not drawn to scale, but rather to highlight major features of the invention.

[0025] The semiconductor integrated circuit is formed on a semiconductor substrate being a part of a so-called semiconductor wafer. This substrate may be doped P+ or doped N+.

[0026] The semiconductor wafer has a face side surface which is still raw, since it is intended to receive the layout of a device or an electronic circuit integrated monolithically in the semiconductor.

[0027] The semiconductor wafer also has an underside surface, oppositely located from the face side surface. These face side and underside surfaces will also be referred to hereinafter as the front and the back of the semiconductor wafer.

[0028] Advantageously in the method of this invention, the surface of the Al alloy metal layer 1 is modified by application of a process step to the semiconductor wafer after completing the processing steps.

[0029] The wafer front is covered with the aluminum metal layer, while its back is deposited a metallization layer comprising plural layers (e.g., TiNiAu).

[0030] The method of this invention leaves the surface of the metal layer on the wafer back unaltered, or at least will not "degrade" it. Accordingly, it allows all of the subsequent processing steps, such as the die-attach process for bonding to the supporting frame used at the packaging stage, to be carried out as normal.

[0031] Advantageously in the method of this invention, a very thin phosphate layer or film 3 is provided which is effective to resist corrosion/hydroxidation of the metal as the latter undergoes stresses in a damp environment. Preferably, this thin film 3 is grown by a chemical surface treatment of the Al alloy metallization layer 1.

[0032] According to the invention, two different classes of chemical surface treatments of the Al layer are provided which are effective to produce a very thin

phosphatised passivating layer exhibiting an anti-corrosion property in a damp environment.

[0033] In essence, the method of this invention can be defined by a first embodiment and a modification thereof, both embodiments falling within the scope of the invention.

[0034] In a first embodiment, the surface of the metal layer 1 is subjected to a two-stage chemical treatment using a mixture of concentrated (100%) nitric acid and trace phosphoric acid.

[0035] A flow chart of this first embodiment of the inventive method is given herein below.

Step 1) Dipping or wetting the wafer in/with concentrated nitric acid ( $\text{HNO}_3$ ):

temperature -- 40 to 50°C;  
time -- at least 10 minutes.

Step 2) Dipping or wetting the wafer in/with a mixture of  $\text{HNO}_3$  and trace phosphoric acid ( $\text{H}_3\text{PO}_4$ ), e.g. 0.005 to 0.01% v/v phosphoric acid:

temperature -- 40 to 50°C;  
time -- 10 to 20 minutes.

This step is to follow Step 1 immediately.

[0036]

Step 3) Post-treatment ultrasonic washing in water.

Step 4) Drying at a low temperature.

[0037] In this first embodiment of the inventive method, the metal layer is coated with a thin protective phosphate film 3.

[0038] However, difficulties may be encountered in implementing the treatment, essentially as follows:

the treatment is highly aggressive because of the elevated temperature of the nitric acid, which mandates the availability of special equipment;

the treatment is not fully compatible with a composite wafer back metallization (e.g. of the TiNiAu type), so that the method steps are best carried out before finishing the wafer back.

[0039] To overcome these difficulties, the invention provides a simpler treatment for the semiconductor wafer, so as to make the method readily integratable and compatible with the process of fabricating the integrated circuit in a wafer.

[0040] In this modified embodiment, the wafer is treated with a mixture of a polar organic solvent, e.g. acetonitrile or ethyl acetate, and phosphoric acid or

phosphate derivatives thereof, at a temperature in the 25 to 40°C range for a time between 5 and 40 minutes. The process sequence and details of the various steps are given herein below.

Step 1) Dipping the wafer in a mixture of polar organic solvent and a small proportion of phosphoric acid ( $\text{H}_3\text{PO}_4$ ), e.g. 0.5 to 1% v/v phosphoric acid. Alternatively, the phosphate reactant is orthophosphoric acid or  $\text{R-H}_x\text{PO}_y$ , where R is an alkaline-type ion group or an alkyl radical:

temperature -- 25 to 40°C;

time -- 5 to 40 minutes.

Step 2) Post-treatment ultrasonic washing in alcohol or water.

Step 3) Drying at a low temperature.

[0041] Before applying the treatment according to this modification of the method, the surface of the metallization layer 1 is coated with a thin (30 to 40Å) layer 2 of native oxide hydrate  $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ . The chemical reactions that take place on this surface during the first step of the inventive method are illustrated by Figures 1A and 1B.

[0042] In a further modification of the inventive method, the aluminum surface, as coated with the thin phosphate film 3 during the previous process steps (1), (2) and (3), is further treated thermally under an  $\text{N}_2$  medium at a temperature of 125° to 150°C for about 1 hour.

[0043] This additional step allows the phosphatised termination to be rebuilt by the formation of a layer of  $\text{AlPO}_4$  phosphate precipitate, which is highly resistant to stress in hot steam. This conclusion is reached following an analysis of the XPS data presented on the respective graphs, discussed hereinafter with reference to Figures 2 to 5.

[0044] The last-mentioned thermal treatment results in the formation of a phosphate layer a few monolayers thick, either partly or fully cured. At this phosphate layer, the thickness of the dehydrated terminating alumina is less than the original one and attains a steady-state value which will depend on the treatment temperature. A possible process marker is provided by ESCA measures which characterize the surface chemistry in terms of both phosphorus content and thickness of the surface aluminum oxide. Figures 2 and 3 relate, for example, to the surface soon after growing the thin film 3 on the semiconductor wafer, and Figures 4 and 5 relate to results obtained by opening mechanically a previously packaged device in plastics of an epoxy resin.

[0045] More particularly, Figures 2 and 4 show the XPS spectrum for the aluminum, wherein the traces of

the aluminum metal and the oxidised aluminum are to be seen. Figures 3 and 5 contain the phosphorus trace.

[0046] The method of this invention does solve the technical problem and offers several advantages, outstanding among which is the fact that the protective phosphate layer actually prevents corrosion of the underlying metallization layer when placed in a damp environment.

[0047] Furthermore, in the specific field of semiconductor integrated devices, the protective layer provided by the method of this invention enables direct bonding of the lead wires to the modified aluminum surface.

#### Claims

1. A protective inhibitor layer of moisture-generated corrosion for aluminum (Al) alloy metallization layers (1), particularly in semiconductor electronic devices, characterized in that it is a thin phosphate layer (3). 20
2. A protective layer according to Claim 1, characterized in that it is a passivating layer.
3. A protective layer according to Claim 1, characterized in that it is grown by chemical treatment of the surface of the Al alloy metallization layer (1). 25
4. A protective layer according to Claim 1, characterized in that it is formed on top of a thin layer (2) of native aluminum oxide hydrate  $Al_2O_3 \cdot xH_2O$ . 30
5. A protective layer according to Claim 1, characterized in that it comprises an aluminum phosphate ( $AlPO_4$ ). 35
6. A protective layer according to Claim 1, characterized in that it is further cured.
7. A method of producing a protective inhibitor layer of moisture-generated corrosion for aluminum (Al) alloy metallization layers (1), particularly in semiconductor electronic devices, characterized by chemically treating the metallization layer (1) in at least two steps using a mixture of concentrated nitric acid and trace phosphoric acid. 40
8. A method according to Claim 7, characterized in that it comprises a first step of dipping the electronic device in concentrated nitric acid ( $HNO_3$ ) at a temperature of about 40° to 50°C for at least ten minutes. 50
9. A method according to Claim 7, characterized in that it comprises a second step of dipping the electronic device in a mixture of nitric acid ( $HNO_3$ ) and trace phosphoric acid ( $H_3PO_4$ ) at a temperature of about 40° to 50°C for 10 to 20 minutes. 55
10. A method according to Claim 9, characterized in that the amount of trace phosphoric acid is of about 0.005 to 0.01% v/v.
11. A method according to Claim 9, characterized in that said second step is carried out directly after the first. 5
12. A method according to Claim 9, characterized in that it further comprises a step of ultrasonic washing in water. 10
13. A method according to Claim 12, characterized in that it further comprises a low-temperature drying step. 15
14. A method of producing a protective inhibitor layer of moisture-generated corrosion for aluminum (Al) alloy metallization layers (1), particularly in semiconductor electronic devices, characterized in that it comprises at least one step of dipping the electronic device in a mixture of a polar organic solvent and phosphoric acid ( $H_3PO_4$ ) or phosphate derivatives thereof in low percent amount, or with a phosphate reactant. 20
15. A method according to Claim 14, characterized in that said percent amount of phosphoric acid is about 0.5 to 1% v/v.
16. A method according to Claim 14, characterized in that said phosphate reactant is orthophosphoric acid or  $R-H_xPO_y$ , where R is an alkaline type of ion group or an alkyl radical.
17. A method according to Claim 14, characterized in that it comprises a further step of ultrasonic washing in alcohol or water.
18. A method according to Claim 14, characterized in that said at least one dipping step is carried out at a temperature of approximately 25° to 40°C for about 5 to 40 minutes. 40
19. A method according to Claim 17, characterized in that it further comprises a low-temperature drying step. 45
20. A method according to Claim 14, characterized in that it further comprises a low-temperature drying step.
21. A method according to Claim 14, characterized in that it comprises a further thermal treatment.
22. A method according to Claim 21, characterized in that said thermal treatment is applied under a nitrogen ( $N_2$ ) atmosphere at a temperature of approxi-

mately 125° to 150°C for about one hour.

23. A method according to Claim 14, characterized in that said polar organic solvent is an acetonitrile or ethyl acetate. 5
24. A semiconductor integrated, electronic device, characterized in that it includes at least one protective, corrosion-inhibiting layer as claimed in Claim 1. 10

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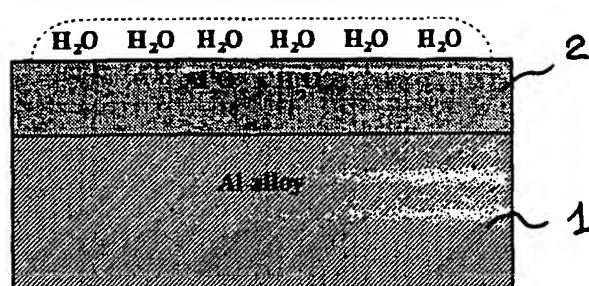


Fig. 1a

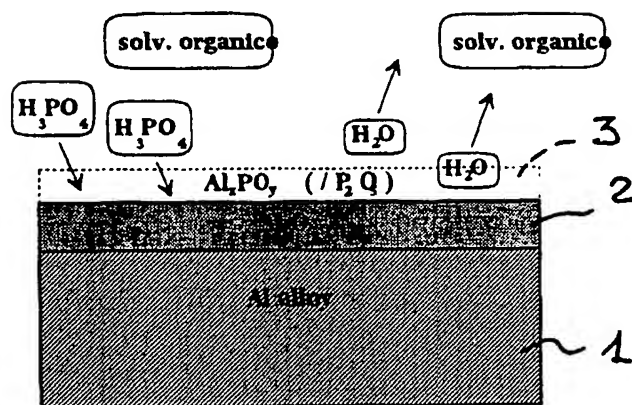


Fig. 1b



Fig. 2

Fig. 3

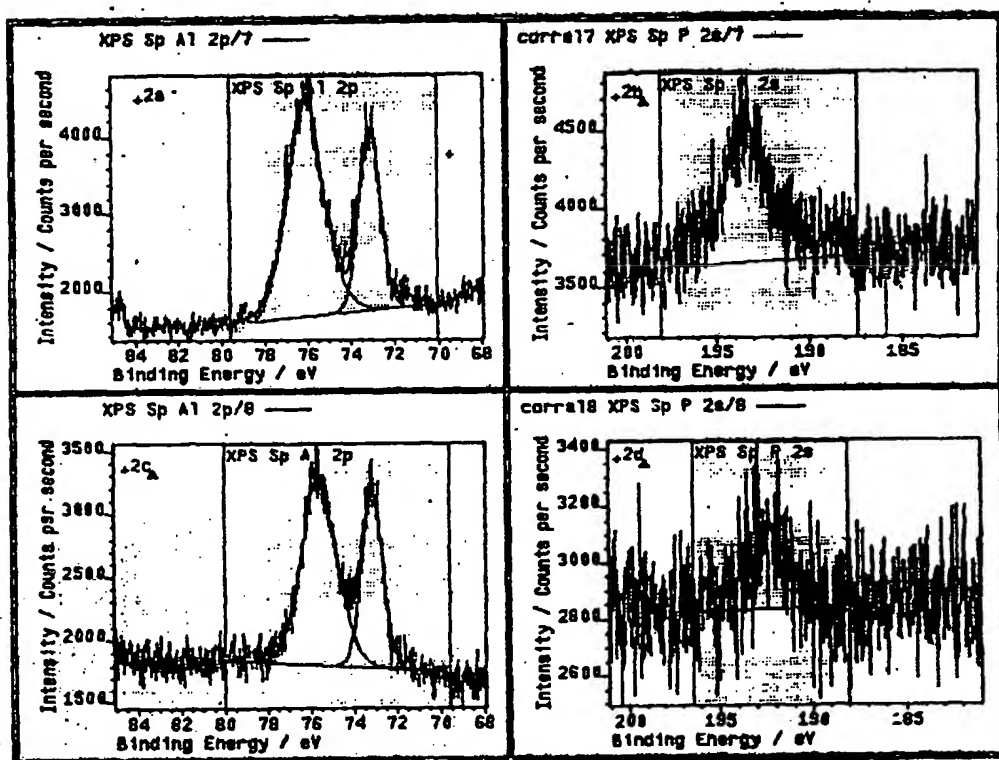


Fig. 4

Fig. 5



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# EUROPEAN SEARCH REPORT

Application Number  
EP 99 83 0718

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The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>19 April 2000</b>	Examiner <b>Torfs, F</b>
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